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Water splitting on Rhodamine-B dye sensitized Co-doped TiO_2 catalyst under visible light

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ABSTRACT

An effective rhodamine B (Rh B) dye sensitized Co doped TiO_2 (Co/TiO_2) materials was prepared by simple physical absorption for photocatalytic water splitting under visible light. The prepared Rh B-Co/TiO_2 materials showed a strong absorbance edge band in the range of 450–600 nm (max. absorbance at 550 nm) and estimated a moderate band gap of 2.58 eV, which lowered than that of Co/TiO_2 (2.75 eV). Rh B-Co/TiO_2 catalysts showed the high activity towards photocatalytic water splitting under visible light irradiation. The reaction with Rh B-Co/TiO_2 catalysts achieved a nearly stoichiometic evolution of H_2 and O_2 evolution of ~227.3 μmol/g-catal/h and ~98.9 μmol/g-catal/h, respectively, which is 6 times higher than that of H_2 evolution (~37.67 μmol/g-catal/h) over Co/TiO_2 catalysts. The enhanced water splitting reaction may be facilitated by the absorbed Rh B near to Co atom. This synergic effect between the Rh B and Co is crucial to the water splitting reaction.

1. Introduction

Water splitting to produce hydrogen and oxygen under visible light radiation will be one of the promising hydrogen production methods because of its cheap production cost, if it is successfully developed the active photocatalysts under visible light. The energy storage capacity of H_2 per gram (119,000 J/g) is three times larger than the storage capacity of oil (40,000 J/g). Expensive and highly sophisticated technologies such as petroleum and steam methane reforming processes are popular for the hydrogen production in large scale [1,2]. Based on one report, water electrolysis process covers only 5% of the commercial hydrogen, while most of hydrogen production (95%) is still covered by reforming of fossil fuels [3]. Contrary, the photocatalytic water splitting process is extensively studied for the hydrogen production from the decomposition of water under UV/visible light illumination in the presence of inorganic semiconducting materials [4,5]. Recently, Domen's group demonstrated reasonably high H_2 gas evolution (16.2 mmol in 35 h) from pure water with gallium and zinc nitrogen oxide catalysts $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ under visible light [6]. In order to find the suitable visible light active catalysts, the large band gap semiconductor materials coupled with to narrow energy band gap semiconductors and doping metals or nonmetals are possibly extend the absorption edge in visible region [7–10]. In our previous work, Yang et al. prepared a hydrothermally synthesized platinum doped titania nanotubes as visible active catalysts and exhibited moderate H_2 evolution of 14.6 μmol/h from water under visible light [11]. To enhance the visible light harvesting efficiency, dye sensitization on semiconductor materials has been recently studied for hydrogen production from water [12,13]. TiO_2 nanomaterials are one of the most popular and interesting semiconductor oxides for photocatalytic water splitting due to its high catalytic, photostability, chemical stability and nontoxic nature [14]. However, its large band gap energy (3.2 eV) limits the utilization in the photocatalytic water splitting under visible light irradiation [15].

Recently, TiO_2 and metal doped TiO_2 nanomaterials have been sensitized by various dyes such as Eosin Y [16], merocyanine [17], $Ru(bpy)_3^{2+}$ [18] and coumarin [19] for hydrogen evolution under visible light. Subramanian et al. has investigated the photocatalytic activity of Co-doped TiO_2 films under visible illumination [20], but the Co-doped TiO_2 has not shown reasonable photocatalytic activity for water splitting to produce H_2 and O_2. However, rhodamine B (Rh B) is one of the important representations of xanthene dyes and well known as a dye laser material for its good stability [21]. In this paper, we have prepared Co doped TiO_2 nanomaterials by impregnation method and sensitized by Rh-B for photo-catalytic

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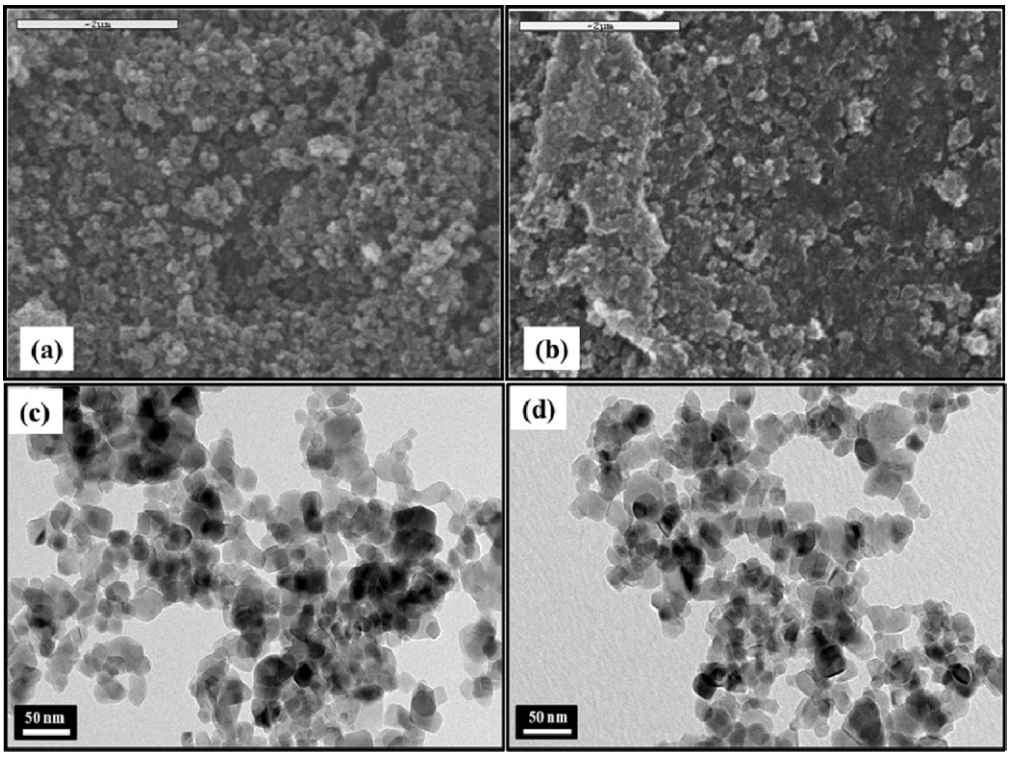

Fig. 1. SEM (a and b) and TEM (c and d) images of Co/TiO_2 (a and c) and Rh B-Co/TiO_2 (b and d), respectively.

water splitting of pure water under visible light. There is no report on the photocatalytic water splitting over the RhB-Co/TiO_2 under visible light irradiation. The photocatalytic water splitting results shows that Rh B-Co/TiO_2 materials confers a highly active in visible light to evolve the stoichiometric H_2 (~227.3 μmol/g-catal/h) and O_2 (~98.9 μmol/g-catal/h) gases from the pure water, respectively.

2. Experimental

The Co doped TiO_2 catalysts were prepared by impregnation method with TiO_2 powders (P-25, Degussa) and $Co(NO_3)_2{\cdot}9H_2O$ as precursors [22]. The desired amount of TiO_2 powder was suspended in distilled water and various amounts of $Co(NO_3)_2{\cdot}9H_2O$ (0.1 M, Aldrich Chemical analytical grade) were added. Then, the suspension was stirred at room temperature for 1 h and evaporated to dry at 80 °C. After washing several times by distilled water to remove unbound cobalt, the Co doped TiO_2 sample was calcined at 450 °C for 2 h, which denoted as Co/TiO_2. For the preparation of Rh B dye sensitized Co/TiO_2, the Rh B dye was absorbed on Co/TiO_2 (1 g) in a mixture of Rh B (1 mmol) and 70 ml of DEA (15% (v/v)) – water solution at room temperature for overnight in the dark [23]. The dye-absorbed sample was washed by acetone and dried at 40 °C under N_2 atmosphere under dark. Thus, the prepared sample donated as Rh B-Co/TiO_2.

The prepared catalysts were characterized by X-ray diffraction (XRD) using a Rigaku diffractometer with Cu Kα radiation (40 kV, 30 mA, scan speed at 6° min^{-1} and the range of 20–80°), scanning electron microscope (SEM, JEOL-JSM 6400, Japan), transmission scanning microscopy (TEM, JEOL, JEM – 2010), Raman Spectroscopy (RFS-100S, Germany) and ultraviolet–visible diffuse reflectance spectroscopy (UV-vis DRS, Shimadzu-UV3600).

Photocatalytic water splitting experiment was carried out in an outer irradiation Pyrex cell under visible light. The Rh B-Co/TiO_2 catalyst powder (50 mg) was dispersed in 70 ml of pure H_2O solution by a magnetic stirrer and an ultrasonic bath for 10 min. A reaction suspension was purged and bubbled by ultra-pure argon gas until no detectable desolved oxygen in the solution before starting the reaction by visible light illumination. The visible light source used ozone-free Xe arc lamp (300 W, Hamamatsu: L 2479) attached with UV cut filter (FSQ-GC 400). The evolved amount of H_2 and O_2 were analyzed by gas chromatography (GC) equipped with a thermal conductivity detector (TCD) and a molecular sieve 5 Å column (stainless steel, 6 ft × 1/8″ OD, Ar as carrier gas). The desorption of RhB dye was carried out by collecting the 2 ml of mixture solution from the water splitting reactor and then measured absorbance of collected samples by the UV-Vis spectrophotometer (Shimadzu-UV3600).

3. Results and discussion

The surface morphologies of Co/TiO_2 and Rh B-Co/TiO_2 are characterized by SEM and TEM as shown in Fig. 1. Co/TiO_2 (Fig. 1 a and c) exhibits small spherical particles with size of 20–25 nm. There are no significant differences in the morphology and size of TiO_2 and Co metal clusters after introducing Rh B on Co/TiO_2 as shown in Fig. 1(b and d). The composition of prepared catalysts is examined by electron dispersive X-ray spectrometer (EDS) coupled in scanning electron microscope (SEM) and the result is summarized in Table 1. The amount of Co metal before (1.52 wt%) and after (1.46 wt%) Rh B dye absorption is very similar, indicating that Rh B dye does not affect the morphology of Co/TiO_2.

XRD patterns of TiO_2, Co/TiO_2 and Rh B-Co/TiO_2 catalysts are shown in Fig. 2. TiO_2 (P25) possesses typically both anatase and rutile phases with 2θ peaks at 25.2, 27.4, 36.2, 37.7, 41.3, 48.0,

Table 1
Summary of EDX analysis of Co/TiO_2 and RhB-Co/TiO_2 photocatalyst.

Elements (wt%)	Co/TiO_2	RhB-Co/TiO_2
C	–	2.24
Ti	58.64	55.24
O	39.84	41.06
Co	1.52	1.46

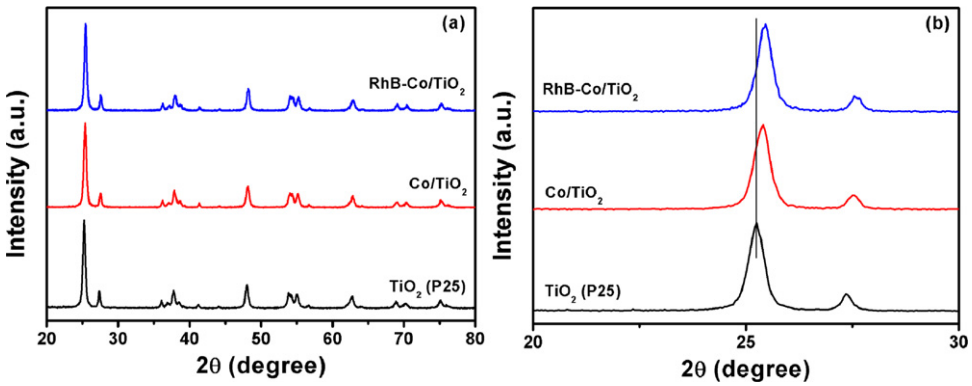

Fig. 2. The broad scale (a) and (b) small scale XRD patterns of bare TiO_2, Co/TiO_2 and RhB-Co/TiO_2 catalysts.

53.8, 55.0, 56.7, 62.6, 68.8 and 75.1°. The XRD peaks are significantly shifted by 0.2° from their original position after doping of Co into TiO_2 as shown in Fig. 2(b). However, there are no XRD peak and TEM image corresponding to Co metal clusters and cobalt oxide, indicating that the most of Co is substituted to the Ti lattice site without any aggregation of Co metal clusters on exterior TiO_2 surface. This Co substitution phenomenon has been reported elsewhere [24]. RhB-Co/TiO_2 exhibits the similar XRD patterns of Co/TiO_2, which suggests that RhB dye absorption does not affect the phases of Co/TiO_2. Thus, the slight shifting in XRD peak clearly indicates the Co doping into the TiO_2 nanomaterials.

Fig. 3 shows UV–vis diffuse reflectance spectra (UV–vis DRS) of Co/TiO_2 and Rh B-Co/TiO_2 catalysts. Co/TiO_2 reveals an absorption edge shifting towards the lower energy region, corresponding to higher wavelength side of the spectra in the visible range (Fig. 3). However, the Rh B-Co/TiO_2 catalyst shows a longer shift with the strong peak in the wavelength of 500–600 nm, which indicates the absorption of Rh B dye on Co/TiO_2 catalyst. The absorption edge of Co/TiO_2 is at ~450 nm, which corresponds to band gap energy of 2.75 eV. Whereas Rh B-Co/TiO_2 reveals a band gap of 2.58 eV, which is significantly lower than those of Co/TiO_2 and TiO_2 (3.2 eV). These results are comaparable to reported studies on metal-doped TiO_2 catalysts [25,26]. The reduction potential of Co^{2+}/Co (−0.27 V at 25 °C) is more positive than that of TiO_2 conduction band energy level (−0.52 V) [27]. Thus, the electrons transfer from the conduction band of TiO_2 to the Co^{2+} ion suppresses the back electron transfer reaction with the holes in the valence band of TiO_2, which cause the low stoichiometric efficiency in the most of photo-catalytic reaction. Additionally, Co^{2+} is a colored ion, which acts as a chromophore and can easily absorbs light in the visible range [28] and Rh B dye sensitization on Co/TiO_2 may be enhanced the light absorption and leads the high light harvesting efficiency in the visible region as compared to TiO_2 and Co/TiO_2 catalyst. Fig. 4(a) shows the amount of absorbed Rh B dye on Co/TiO_2 as a function of dye absorption time. The Rh B dye absorption on the surface of Co/TiO_2 increases as increasing the time and reaches equilibrium to ~25.06 μmol-Rh B/g-catal after 24 h.

Fig. 5 presents the accumulated hydrogen and oxygen evolution from pure water solution containing suspensions of bare TiO_2, Co-TiO_2 and Rh B-Co/TiO_2 under visible light irradiation ($\lambda \geq 420$ nm)

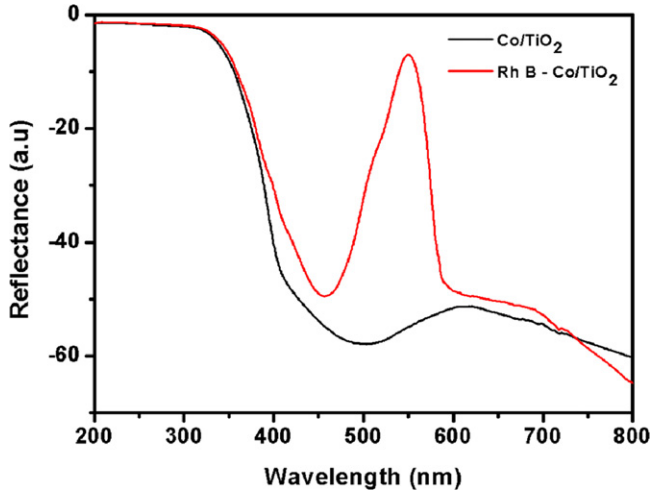

Fig. 3. UV–vis DRS of Co/TiO_2 and Rh B-Co/TiO_2 catalysts.

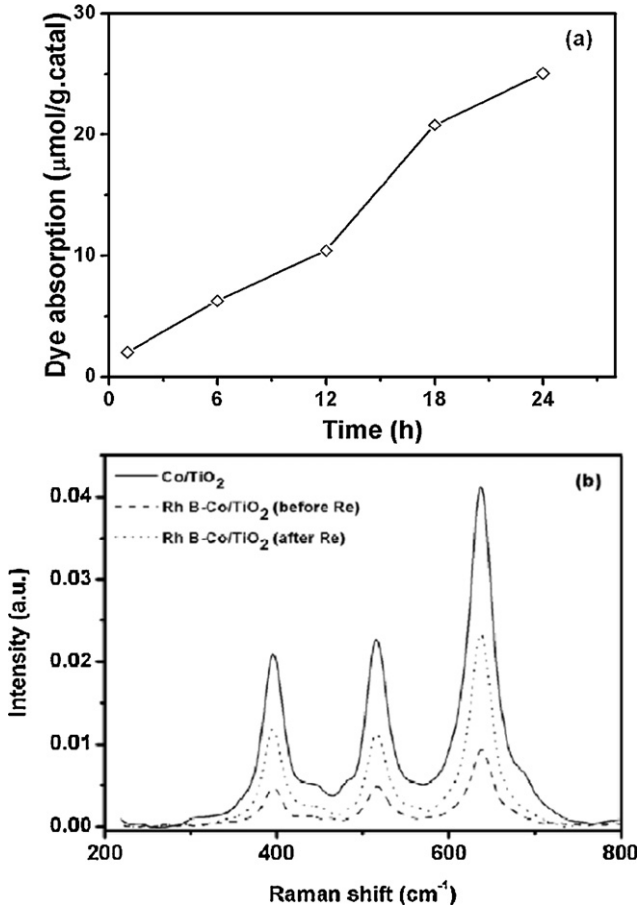

Fig. 4. (a) The rate of Rhodamine B dye absorbed on the surface of Co/TiO_2 catalyst and (b) Raman spectra of Co/TiO_2, Rh B-Co/TiO_2 materials before and after reaction.

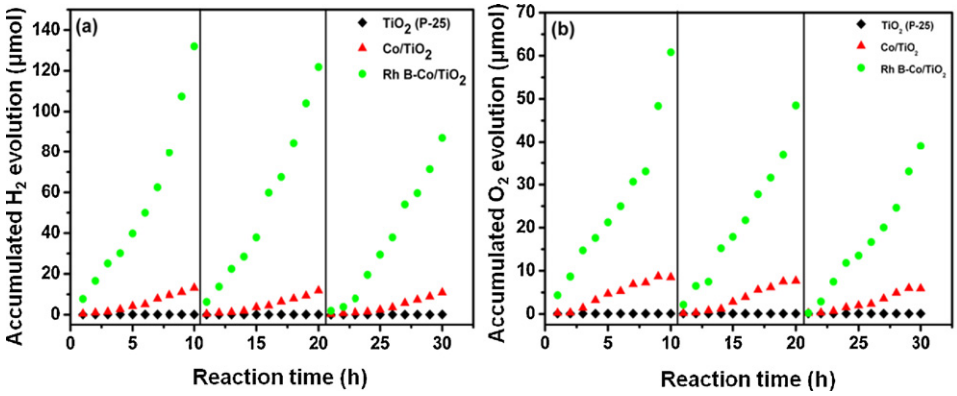

Fig. 5. (a) Accumulated hydrogen and (b) oxygen evolution as a function of reaction time over Rh B-Co/TiO_2, Co/TiO_2 and TiO_2 photocatalysts.

with repsect to reaction time and summarizes in Table 2. Rh B-Co/TiO_2 catalyst obtains significantly high rates of accumulated H_2 and O_2 evolution of ~227.3 (μmol/g-catal/h) and ~98.9 (μmol/g-catal/h), respectively, which shows a nearly schiotometric ratio of gas evolution from water. When the light turns off, no H_2 and O_2 evolution observe, indicating that the reaction is induced by the absorption of visible light and not by any tribological or mechanical processes. Moreover, the photocatalytic reaction of water splitting has been performed with only Rh B under visible light, which shows no H_2 and O_2 production, indicating that RhB dye needs a supportive surface for generating the reduction sites of water splitting under visible light irradiation. With RhB-Co/TiO_2 photocatalyst, the rate of hydrogen evolution to absorbed dye is estimated ~9.07 H_2/dye/h. However, Co/TiO_2 catalyst shows relatively very low production rate of accumulated H_2 (~37.67 μmol/g-catal/h) and O_2 (~12.6 μmol/g-catal/h) and no visible activity is observed on TiO_2 catalyst. Rh B-Co/TiO_2 catalyst is 6 times active than Co/TiO_2 catalyst in terms of water splitting under visible light.

The absorbed dye on Rh B-Co/TiO_2 catalyst was gradually desorbed and turned the solution to slightly red color of Rh B as a function of reaction time. Fig. 6 shows the comparative study of amount of accumulated H_2 and O_2 gas evolution and the amount of desorbed dye on Rh B-Co/TiO_2 in the reaction time. The amount of desorbed Rh B dye increased to ~50% after 3 h and ~80% after 7 h and then reach the platue of the desorbed amount at around 80%. The accumulated H_2 and O_2 gas evolution gradually increases as increasing the reaction time, even though significant desorption of Rh B, as shown in Table 3. Interestingly, the H_2 gas evolution per the number of dye per hour is almost constant, ~9.07 H_2/dye/h in the overall range of reaction time. This suggests that water splitting reaction may be facilitated by the remained ~20% Rh B (~5 μmol-Rh B/g-catal) which is close to Co atom. However, around 80% absorbed Rh B to Ti atom and far from Co atom may not involve in the photocatalytic reaction. This synergic effect between the Rh B and Co is crucial to proceed the water splitting reaction under visible light.

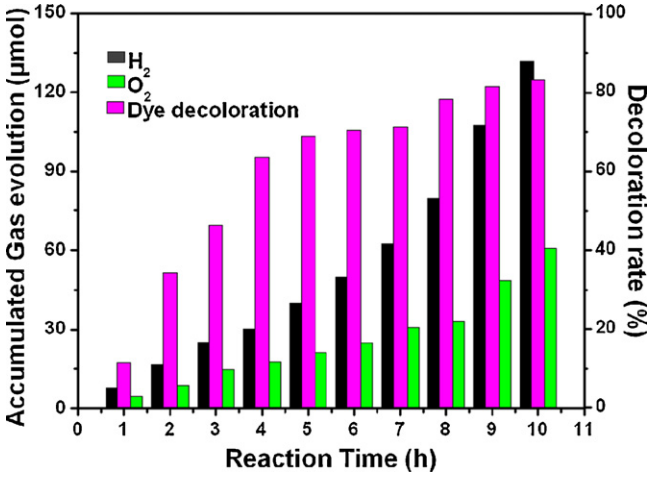

Fig. 6. Amount of accumulated hydrogen, oxygen evolution and desorption of Rh B dye as a function of reaction time.

Fig. 4(b) exhibits the Raman spectra of Co/TiO_2 and Rh B-Co/TiO_2 catalysts before and after reaction. All samples show the three Raman peaks in the range of 300–800 cm^{-1} that represent the typical crystal structure of TiO_2 materials. After the Rh B absorption, the intensity of Raman shift is decreased as compared to Co/TiO_2, indicating the attachment of Rh B dye with Co/TiO_2 materials. The intensity of Raman shift is smaller than those of Rh B-Co/TiO_2 and Co/TiO_2 catalysts after water splitting reaction, which demonstrates the lowering in the crystallinity of Co/TiO_2. It may due to the detachment of Rh B dye on the surface of Rh B-Co/TiO_2. This result indicates the absorption of Rh B absorption over the surface of Co/TiO_2 promotes the photocatalytic water splitting reaction under visible light inspite of detachment of Rh B dye from the catalyst after reaction.

Rh B dye in Rh B-Co/TiO_2 photocatalytic improves the light harvesting of water splitting reaction as illustrated in Fig. 7. Under visible light illumination, the absorbed dye molecule directly

Table 2
Accumulated H_2 and O_2 gas evolution in the photocatalytic water splitting over TiO_2, Co/TiO_2 and Rh B-Co/TiO_2 under visible light.

Time (h)	TiO_2 (μmol)		Co/TiO_2 (μmol)		Rh B-Co/TiO_2 (μmol)	
	H_2	O_2	H_2	O_2	H_2	O_2
1	0.10	0.1	0.5	0.25	7.7	21.3
2	0.10	0.1	1.02	0.31	16.7	60.9
4	0.103	0.1	2.6	1.4	30.2	78.7
6	0.11	0.1	5.2	2.7	49.9	109.4
8	0.11	0.1	9.6	5.3	79.6	122.5
10	0.114	0.1	13.2	8.1	132.0	148.5

Table 3
Accumulated H_2 evolution and dye desorption (%) in the photocatalytic water splitting over the surface of Rh B-Co/TiO_2 catalysts.

Reaction time (h)	Desorption of dye (%)	Acumulated H_2 (μmol)
1	3.6	7.7
2	11.5	16.7
4	39.5	30.2
6	63.6	49.9
8	78.3	79.6
10	83.1	132.0

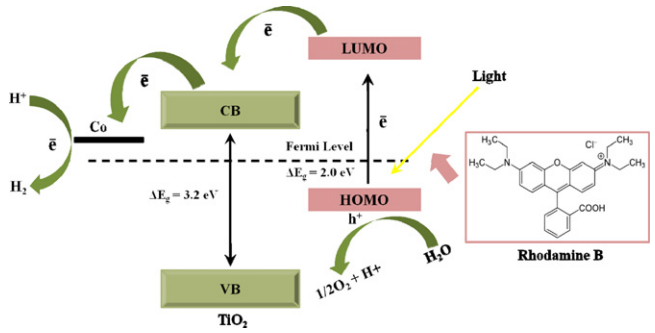

Fig. 7. The schematic illustration of water splitting over Rh B-Co/TiO_2 photocatalysts under visible light.

injects electron to Co metal as well as to the conduction band of TiO_2 and leaves the hydrogen and molecular oxygen radicals/ions at Co^{2+} ions which are closely related to better efficiency of hydrogen evolution. In case of Rh B-Co/TiO_2, the H_2 evolution is higher than Co/TiO_2 and TiO_2 due to the efficient electron transfer from dye to Co via TiO_2. It has been reported that noble metal loading into TiO_2 materials invokes absorption of dye and charge separation of $\bar{e}$–h^+ pairs, which affects the performance of hydrogen evolution from H_2O due to the synergic effect [29,30]. Therefore, the prepared Co/TiO_2 catalysts may significantly increases the Rh B dye absorption and charge separation of $\bar{e}$–h^+ pairs in Rh B-Co/TiO_2 catalyst, resulting in the high H_2 evolution as compared to Co/TiO_2 under visible light illumination as depicted in Fig. 6. In order to investigate the role of Co metal, a parallel study has been carried out for photocatalytic water splitting over only Rh B-TiO_2 catalyst under the visible light illumination. Hydrogen evolution is not detected on Rh B-TiO_2 catalyst. Moreover, it could expect that band gap energy of TiO_2 is not enough to transfer hole from the valance band to oxidized Rh B dye for the regeneration. Thus, the presence of Co^{2+} ions on surface of TiO_2 is crucial for facilitating electron transfer to the TiO_2 conduction band and downlift of valance band. Therefore, the Rh B-Co/TiO_2 may be increased the electron transfer and light harvesting efficiency during the water splitting under visible light, resulting in the high accumulated H_2 and O_2 evolution.

4. Conclusion

The sensitization of Rh B dye over the surface of Co/TiO_2 was carried out by simple physical absorption followed Co impregnation into TiO_2 materials for photocatalytic water splitting under visible light. The prepared Rh B-Co/TiO_2 materials showed a strong visible absorbance edge band in the range of 450–600 nm (max. absorbance at 550 nm) and slightly lowered band gap of 2.58 eV as compared to Co/TiO_2 (2.75 eV) and TiO_2 (3.21 eV). From photocatalytic water splitting results, Rh B-Co/TiO_2 catalysts showed the stoichiometic evolution of H_2 and O_2 gas of ~227.3 μmol/g-catal/h and ~98.9 μmol/g-catal/h, respectively, which was 6 times higher than that of H_2 evolution (~37.67 μmol/g-catal/h) with Co/TiO_2 catalysts. Interestingly, the accumulated H_2 and O_2 gas evolution was proportional to the water splitting reaction time even though continuous desorption of Rh B up to 80% after 8 h. However, the H_2 gas evolution per the number of dye per hour is almost constant, ~9.07 H_2/dye/h, in the overall range of reaction time. Conclusively, the water splitting reaction may be facilitated by the remained ~20% Rh B (~5 μmol-Rh B/g-catal) which may close to Co atom. Around 80% absorbed Rh B to Ti atom far from the Co atom may not involve in the photocatalytic reaction. This synergic effect between the Rh B and Co is crucial to enhance the water splitting reaction.

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